U.S. DEPARTMENT OF COMMERCE

PB80-177017

Photoreactivity of Aquatic Pollutants Sorbed on Suspended Sediments

(U.S.) Environmental Research Lab.
Athens, GA

Jul 79

U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/J-79-067	2. JOURNAL ARTICLE
3. REC	PB80-177017
4. TITLE AND SUBTITLE: Photoreactivity of Aquatic Pollutants Sorbed on Suspended Sediments	5. REPORT DATE
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S): Glenn C. Miller and Richard G. Zepp	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, Georgia 30605	10. PROGRAM ELEMENT NO. 1HE775
	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS: U.S. Environmental Protection Agency--Athens, Georgia, Environmental Research Laboratory, College Station Road, Athens, Georgia 30605	13. TYPE OF REPORT AND PERIOD COVERED: Journal article
	14. SPONSORING AGENCY CODE: EPA/600/01

15. SUPPLEMENTARY NOTES

Environmental Science & Technology July 1979 860-863 Contact: R.G. Zepp, 250-3428

16. ABSTRACT

A technique is described that can be used to ascertain the photoreactivity of chemicals sorbed on particulates suspended in water. The influence of sorption on photoreactivity is disentangled from the effects of light attenuation and scattering by the sorbent. When this technique was employed, the photoreactivity of two hydrophobic chemicals was determined on sediments obtained from three widely separated water bodies in the United States. Kinetic and product studies indicate that the sorbed chemicals are in a less polar microenvironment that is a considerably better hydrogen atom donor than water.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Photolysis Mathematical models	Aquatic systems Natural waters Solar photolysis Sediment	07D 07E 06F 13B 18B 68D

18. DISTRIBUTION STATEMENT: RELEASE TO PUBLIC	19. SECURITY CLASS (This Report): UNCLASSIFIED
	21. NO. OF PAGES: 6
	20. SECURITY CLASS (This page): UNCLASSIFIED
	22. PRICE

REPRODUCED BY NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE SPRINGFIELD, VA 22161

Photoreactivity of Aquatic Pollutants Sorbed on Suspended Sediments

EPA-600/J-79-067
JOURNAL ARTICLE

Glenn C. Miller[1] and Richard G. Zepp*

Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, Ga. 30605

■ A technique is described that can be used to ascertain the photoreactivity of chemicals sorbed on particulates suspended in water. The influence of sorption on photoreactivity is disentangled from the effects of light attenuation and scattering by the sorbent. When this technique was employed, the photoreactivity of two hydrophobic chemicals was determined on sediments obtained from three widely separated water bodies in the United States. Kinetic and product studies indicate that the sorbed chemicals are in a less polar microenvironment that is a considerably better hydrogen atom donor than water.

Organic pollutants from municipal, industrial, and agricultural sources are often found in sediment-laden streams and ponds (*1*). In these waters, significant fractions of extremely hydrophobic pollutants are physically sorbed to the suspended sediments (*2–4*). Several studies have indicated that the photochemical behavior of chemicals in the sorbed state differs from that in the dissolved state (*5, 6*), but few studies have been conducted using commercially important chemicals or natural sediments. Bailey and Karickhoff (*7*), however, found that the electronic absorption spectra and photochemistry of the pesticide paraquat and *N*-methylpyridinium cation were greatly altered by sorption on clays suspended in water. Carey and co-workers (*8*) observed that polychlorinated biphenyls were photodechlorinated rapidly when sorbed on suspended titanium dioxide in water. Polycyclic aromatic hydrocarbons are photoreactive when sorbed on garden soil (*9*) or on kaolinite or calcium carbonate suspended in water (*10, 11*). Although these studies have provided interesting qualitative data concerning heterogeneous photolysis in water, no quantitative studies of these phenomena have been conducted.

In an earlier paper (*12*), data were presented concerning the effects of natural sediments on photolysis rates of dissolved pollutants. The primary effect noted was a decrease in the photolysis rate caused by light attenuation by the sediment. Under certain conditions, however, the increased diffuseness of light that was caused by light scattering actually resulted in enhanced photolysis rates in clay suspensions. Effects of light attenuation and scattering must be taken into account to quantitatively determine the photoreactivity of a chemical that is sorbed in a heterogeneous system. The present work describes a procedure that was employed to ascertain the photoreactivity of two hydrophobic organic chemicals sorbed on natural sediments suspended in water.

Experimental

Materials. Suspensions of sediments were obtained by resuspending bottom sediment from three natural sources in tap water. Because it was necessary to maintain stable suspensions over the course of the experiments, each sediment suspension was allowed to settle for 24 h and only the supernatant (top 10 cm) was used. According to Stokes law (*13*), this supernatant contained particles with diameters less than approximately 2 μm.

γ-Methoxy-*m*-trifluoromethylbutyrophenone (MTB) was synthesized by the procedure described by Wagner and coworkers (*14*) and was purified by vacuum distillation (bp 86–87 °C, 1 mm): mass spectrum no parent, *m/e* 188, 173, 145, 59 (base); NMR 1.9 (p, CH_2), 3.2 (s, CH_3), 2.8–3.6 (two q, CH_2), 7.3–8.2 (m, Ph). *m*-Trifluoromethylpentadecanophenone (TPP) was similarly synthesized and was purified by column chromatography on silica gel (mp 29–30 °C); mass spectrum *m/e* 370 (parent), 188 (base), 173, 145, 57, 55.

3,4-Dichloroaniline (DCA) was obtained from Aldrich Chemical and recrystallized three times from 95% EtOH (mp 72 °C). 1,1-Bis(*p*-chlorophenyl)-2,2-dichloroethylene (DDE) was obtained from Aldrich Chemical and used as received. *p,p'*-Dichlorobenzophenone and 1,1-bis(*p*-chlorophenyl)-2-chloroethylene (DDMU) were obtained commercially, and the DDE photoisomers were synthesized as described elsewhere (*15*). The major photoproduct of MTB and TPP, *m*-trifluoromethylacetophenone, was obtained from PCR, Inc., Gainesville, Fla. The cyclobutanol photoproducts derived from TPP were synthesized by direct photolysis of TPP in argon-saturated benzene (*16*). Mass spectra of the cyclobutanols were obtained by combined gas chromatography–mass spectrometry. The mass spectra were those expected for trifluoromethyl-substituted phenylcyclobutanols, i.e., weak M − 18 and M − 28 fragments as well as an intense ion at *m/e* 188 (*16*). On a 3% SP-2250 column, the two cyclobutanols coeluted with retention times slightly shorter than TPP.

Distilled water was purified by distillation from permanganate, and spectroquality organic solvents were obtained commercially.

Equipment. Photochemical rate studies were performed in an apparatus previously described (*17*). This apparatus was employed for simultaneous irradiation of the chemicals in distilled water solutions and in sediment suspensions. Ultraviolet light was derived from a 450-W, medium-pressure mercury vapor lamp. For kinetic studies at 313 nm, the light was filtered through a 3-mm Pyrex glass and a 1-cm solution of 0.001 M potassium chromate in 3% aqueous potassium carbonate. Analysis of the reaction mixtures was performed on a Tracor MT 220 gas chromatograph equipped with a ^{63}Ni electron-capture detector; 2 m long × 2 mm i.d. columns containing 1.95% OV-210–1.5% OV-17, 3% SP-2250, or 3% Silar 5CP on 80/100 Gas-Chrom Q were used.

Procedures. The concentration of suspended sediment was determined by subtracting the concentration of dissolved solids from the concentration of total solids in the suspensions. Dissolved solids for these sediments were less than 10% by weight of the total solids. Organic carbon was determined by Galbraith Laboratory, Knoxville, Tenn.

Addition of each compound to a suspension or solution was accomplished by coating the chemicals on the sides of Erlenmeyer flasks by evaporation of organic solutions. Either sediment suspension or distilled water was then added and stirred overnight (*18*). Solutions in distilled water were centrifuged at 16 000 rpm for 1 h, and solution from the upper third of the centrifuge tube was retained. The concentrations of MTB and DCA in the supernatants of centrifuged sediment suspensions were >95% of the concentrations prior to centrifugation, indicating that these chemicals were predominantly dissolved. To ensure predominant sorption of TPP and DDE on the sediments, the concentrations were adjusted to exceed their water solubilities by factors of 5- to 20-fold and very high sediment concentrations were employed. After centrifugation, the concentrations of TPP and DDE in the supernatants were <5% of their concentrations in the suspensions. The concentrations of all the compounds studied

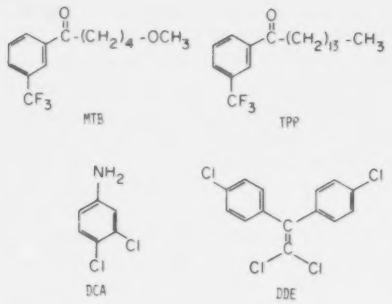
[1] Present address, Division of Biochemistry, University of Nevada, Reno, Nev. 89507.

Published in **ENVIRONMENTAL SCIENCE & TECHNOLOGY,** July 1979, pp. 860–863, by the American Chemical Society

Table I. Sources and Properties of Sediment Suspensions

water body	location	concn, mg/L	pH	organic C, %
Missouri River	northeastern Mont.	520	8.1	0.91
Mississippi River	northwestern Miss.	590	7.5	1.47
Doe Run Pond	Athens, Ga.	275	6.7	3.12

Chart I. Molecular Structures of Chemicals Employed in This Study



were low enough that light absorption by the compounds was negligible compared to light attenuation by water and/or sediment.

Kinetic studies were performed by irradiating the suspensions or solutions (3.00 mL) in glass-stoppered Pyrex 13 × 100 mm culture tubes. Irradiated solutions of MTB, TPP, and DDE were extracted with isooctane; benzene was used for extraction of DCA. Gas chromatography with electron-capture detection was used to analyze the organic layer.

Photoproducts of DDE (20 μg/L) sorbed to Mississippi River sediments were identified by comparing retention times of the products on the GLC columns mentioned above to those of authentic samples (*15*). The photoproducts of TPP did not respond to electron-capture detectors nearly as well as TPP itself. Accordingly, 1-L suspensions of sorbed TPP (100 μg/L) were irradiated (313 nm) to 50% conversion, isooctane extracts of the suspensions were concentrated to 0.1 mL, and the concentrated extracts were analyzed by GLC employing flame detection. Product identifications were made by comparison of retention times with those of authentic samples.

Results and Discussion

Kinetic Studies. Although the majority of nonpolar organic chemicals are not very water soluble, it is now recognized that wide variations exist in the degree of hydrophobicity of such compounds. The tendency of a chemical to sorb on suspended sediments is inversely related to its water solubility (*18*). In designing kinetic studies, we took advantage of the differing sorption tendencies of several organics to disentangle the influence of sorption on photoreactivity from the effects of light attenuation and scattering by the sorbent.

Two pairs of compounds were selected for the study (Chart I). The phenyl ketones, MTB and TPP, were selected because photoreactions of this type of organic compound have been well characterized (*14, 16*). Photolysis yields three major products: an acetophenone derivative and two isomeric phenyl-substituted cyclobutanols. The trifluoromethyl group was built into the compounds to permit analysis at low concentrations using gas chromatography with electron-capture detection. The long tetradecyl chain of TPP rendered it extremely hydrophobic (solubility 25 μg/L at 25 °C), and it had a strong tendency to sorb. On the other hand, MTB was about four orders of magnitude more soluble than TPP (340 mg/L at 25 °C), and even with high concentrations of sediment present, it remained predominantly in the dissolved state (*12*).

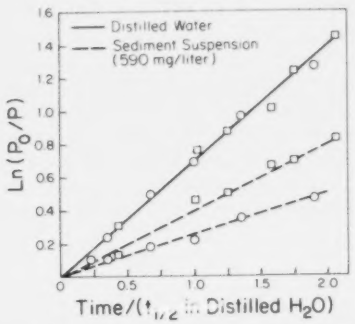


Figure 1. Kinetic data for photolysis (313 nm) of DDE and DCA in distilled water and in suspensions of Mississippi River sediment. The time scales for each chemical were normalized by dividing reaction time by the half-life of the chemical in distilled water: (□) DDE; (○) DCA

Two chlorinated chemicals that are known to be present in the aquatic environment were also studied. The aniline derivative DCA, which is a metabolite of the herbicides diuron and propanil, photoreacts in water with replacement of the *meta*-chlorine by a hydroxyl group (*19*). As with TPP, it had a very low tendency to sorb to suspended sediments. The other chlorinated compound, DDE, is widely distributed in the environment and extremely hydrophobic (solubility 1.3 μg/L, 25 °C). Field studies have demonstrated its great tendency to sorb to sediments (*3*), and, like DCA (*19*), it photoreacts rapidly in sunlight (*15*).

Rather than employing model sorbents such as pure clay minerals for these studies, resuspended bottom sediments from three water bodies in the United States were used (Table I). Sediment concentrations for the experiments ranged from 275 to 590 mg/L, and the sediments were fractionated so that only the clay-sized particles (less than 2 μm) were present in the suspensions. The pH values of the suspensions fell in the 6.7 to 8.1 range.

All four chemicals were irradiated in distilled water and in the sediment suspensions. Monochromatic light (313 nm) was used to facilitate interpretation of the results. In all experiments, the decrease in concentration with time could be described by a first-order rate expression (*20*), i.e., plots of log concentration vs. time were linear (Figure 1).

In the case of the hydrophobic chemicals DDE and TPP, the concentrations of sediment and chemical were adjusted to ensure predominant sorption. The isooctane-extractable portion of these chemicals completely photoreacted with exposure times of 3 h in the photoreactor, demonstrating that it was not protected from the light by sorption. No attempt was made to recover additional amounts of these chemicals by extraction with more polar solvents. The more water-soluble compounds, DCA and MTB, were also photolyzed in the same suspensions that were used with the hydrophobic compounds. It was demonstrated by centrifugation that these chemicals were predominantly dissolved. With all of the compounds, no change in concentration occurred in dark controls. Other control experiments established that the dissolved substances in the sediment suspensions did not photosensitize or quench reaction of DCA and MTB. Thus, the effects noted below are not attributable to alterations in the photoreactivity of the chemicals partitioned in the aque-

Table II. Kinetic Data for Photoreaction of Selected Chemicals in Distilled Water and in Sediment Suspensions at 313 nm[a]

sediment	F_{ws}[b]		F_{is}[c]		PR[d]	
	DCA	MTB	DDE	TPP	DDE	TPP
Missouri River	0.42 ± 0.05	0.37 ± 0.05	0.60 ± 0.25	0.18 ± 0.04	1.5 ± 0.8	0.46 ± 0.16
Mississippi River	0.37 ± 0.02	0.36 ± 0.02	0.56 ± 0.06	0.087 ± 0.02	1.5 ± 0.2	0.24 ± 0.07
Doe Run Pond	0.20 ± 0.02	0.17 ± 0.02	0.31 ± 0.06	0.032 ± 0.005	1.5 ± 0.5	0.17 ± 0.04

[a] Data for each compound are average of duplicate experiments ± range. [b] Ratio of first-order rate constants in sediment suspension to rate constant in distilled water for predominantly (>95%) dissolved chemicals. [c] Same as footnote *b* but for predominantly sorbed chemicals. [d] Photoreactivity ratio defined as ratio of F_{is} to average F_{ws} value for the suspension.

Table III. Photoproducts of DDE under Various Reaction Conditions

reaction medium	% yield[c]		
	p,p'-dichlorobenzophenone	DDMU	*o*-Cl-DDMU
air-saturated water[a]	15	2	20
air-saturated hexane[a]	15	10	20
degassed hexane[a]	0	56	20
sorbed to Mississippi River sediments[b]	5	30	20

[a] Reference *15*. [b] This study. [c] Expressed as percentage of amount reacted.

ous phase of the suspensions.

Ratios of first-order rate constants for photoreaction in the suspensions and in distilled water were determined (Table II). The ratios F_{ws} for the more water-soluble compounds, DCA and MTB, were the same (within experimental error). The sediments slowed their photolysis by light screening. The ratios F_{wi} for the highly insoluble chemicals, DDE and TPP, differed from the F_{ws} values, indicating that factors other than light screening influenced their photochemical behavior. This effect is illustrated by the kinetic data for the Mississippi River sediments (Figure 1). The time scale was normalized so that the kinetic data for DCA could be directly compared to those for DDE; DCA actually photolyzed about three times more rapidly than DDE in water. Note that the photolysis rate constant of DDE in the suspension was not decreased as much as that of DCA, i.e., F_{wi} was larger than F_{ws} for this suspension. The ratio of F_{wi} to F_{ws}, PR, is assumed to be a quantitative measure of the effect of sorption upon the photoreactivity of the hydrophobic chemical (Equation 1):

$$\mathrm{PR} = \frac{F_{is}}{F_{ws}} \tag{1}$$

In other words, it is assumed that the product of F_{ws} and the rate constant for photolysis of the hydrophobic compound in distilled water equals the rate constant for the hydrophobic compound if it were dissolved in the suspension.

Photoreactivity ratios computed by Equation 1 are summarized in Table II. Although considerable experimental error accumulated in the PR values, the data do indicate that DDE is somewhat more photoreactive in the sorbed state than dissolved in water. The data for TPP showed a definite *decrease* in photoreactivity on the sediments.

Interpretation of Kinetic Results. Studies of the sorption of pollutants on suspended sediments have shown that the ability of a sediment to sorb nonpolar organic chemicals is quantitatively related to its organic content (*18*). One interpretation of these results is that the nonpolar organics selectively sorb to the organic components of the sediments. The results of this photochemical study indicate that the sorbed pollutant is probably in an environment similar to a saturated hydrocarbon.

Assuming that only direct photolysis occurs on the sediment surface, PR is defined by Equation 2:

$$\mathrm{PR} = \frac{(\epsilon_s \phi_s)}{(\epsilon_w \phi_w)} \tag{2}$$

where ϵ_s and ϵ_w are molar absorptivities of sorbed and dissolved chemical, respectively, and ϕ_s and ϕ_w are reaction quantum efficiencies in the sorbed and dissolved state, respectively. The PR value for DDE of about 1.5 on all the sediments examined is close to the value of about 1.3 observed for the ratio of photolysis rates of DDE in hexane and water at 313 nm (*15, 20*). Furthermore, the decrease in photoreactivity observed for TPP sorbed to the sediments is consistent with the known drop in reaction quantum efficiencies that occur for phenyl ketones in going from polar to nonpolar reaction media (*16*). It is conceivable that part of the decrease observed with TPP involved physical quenching of its excited state by materials on the sediment surface.

Most revealing were the photoproduct studies, particularly in the case of DDE (Table III). The mechanism for this reaction is discussed elsewhere (*15*). The data in the table indicate that the yield of DDMU is larger in hexane than in water. Formation of DDMU involves "reductive dechlorination", i.e., replacement of a vinyl chlorine by hydrogen. When dissolved air is carefully removed from the hexane by degassing, the yield of DDMU jumps to 56% and the yield of dichlorobenzophenone drops to 0. DDE also reacts to form the photoisomer *o*-Cl-DDMU in about the same yield under all reaction conditions, including when the DDE is sorbed on Mississippi River sediments. These studies indicated that the yield of DDMU is considerably higher on the sediment than in water. In fact, the yield of DDMU was higher on the sediment than in air-saturated hexane, and the yield of dichlorobenzophenone was lower. These results demonstrate that the microenvironment of DDE sorbed on the sediment is a good hydrogen donor, like hexane, but very much unlike water. Moreover, the unexpectedly high yield of DDMU and the low yield of dichlorobenzophenone that formed on the sediment indicate the microenvironment might also be somewhat anaerobic.

Photoproduct studies of TPP sorbed on sediment were less rewarding. It was hoped to learn something about the microenvironment of sorbed TPP by examining the ratio of the two cyclobutanols (*15, 21*); the trans to cis ratio is sensitive to changes in solvent. Unfortunately, the isomers could not be adequately resolved by gas chromatography.

The results of this study differ from findings of other related studies. The photoreactivity and spectra of the cationic chemicals, paraquat and *N*-methylpyridinium cation, are greatly altered when the chemicals are sorbed on soil clays (*7, 22*). That differences occur in the photochemical behavior of

sorbed cationic and nonpolar chemicals can be readily explained in terms of sorption site. The cationic chemicals predominantly adsorb to the clay mineral part of the sediment (*22*), whereas the nonpolar compoun ls associate with the organic part (*18*).

Differences between this study and another recently reported by Hautala (*23*) are more difficult to explain. Hautala found that the photoreactivity of several pesticides was greatly *decreased* compared to aqueous photoreactivity when the pesticides were adsorbed on several different types of soil. The observed effects could not be attributed to light screening; very thin (30-μm thick) soil layers were employed. Moreover, it was also demonstrated that the quantum yield for reaction of DDE, a chemical that exhibited enhanced photoreactivity in this study, was decreased by over two orders of magnitude under Hautala's reaction conditions (*24*), indicating that his results were not a compound-specific phenomenon. It seems unlikely that the observed differences can be attributed to some fundamental difference in the nature of soils and suspended sediments. Most of the sediment in rivers and ponds is derived from soil runoff (*1*). A more likely explanation involves the methods employed to sorb the chemicals on the soil or sediment. With the soil study, solutions of the pesticides dissolved in organic solvents were evaporated to dryness on thin layers of the soil. The pesticide was thus *uniformly* distributed on the soil surface. In this study, the chemicals were first coated on the walls of glass flasks, and then the sediment suspensions were added with stirring. The chemicals gradually dissolved in the water and then sorbed on the suspended sediment. Evidence discussed above suggests that sorption of nonpolar organics from water occurs selectively on the organic part of the sediment. Thus, the two procedures may result in entirely different microenvironments for the sorbed chemicals.

Summary and Conclusions

A procedure is described that can be used to ascertain the photoreactivity of hydrophobic pollutants that are sorbed to sediments suspended in water. The technique was employed to examine the photoreactivity of two hydrophobic chemicals sorbed to natural sediments obtained from water bodies in the United States. Both chemicals exhibited different photoreactivities when sorbed than when dissolved in water, but the changes in photoreactivity were not large. Kinetic and product studies of the photoreactions suggested that the sorbed chemicals are in a nonpolar environment that is a considerably better hydrogen donor than water. Further studies will be required to more clearly elucidate the nature of this environment. Comparison of the results of this and other related studies indicates that the mode of application of the chemical to the surface of a soil or sediment strongly affects its photochemical behavior.

Acknowledgments

We acknowledge the assistance of P. F. Schlotzhauer in conducting the product studies and M. H. Carter in obtaining the mass spectra.

Literature Cited

(1) Wadleigh, C. H., *Soil Conserv.*, **33,** 27 (1967).
(2) Pierce, R. H., Olney, C. E., Felbeck, G. T., Jr., *Geochim. Cosmochim. Acta*, **38,** 1061 (1974).
(3) Miles, J. R. W., *Pestic. Monit. J.*, **10,** 87 (1976).
(4) Herbes, S. E., *Water Res.*, **11,** 493 (1977).
(5) Terenin, A., *Adv. Catal.*, **15,** 227 (1964).
(6) Leermakers, P. A., Weis, L. D., Thomas, H. T., *J. Am. Chem. Soc.*, **87,** 4403 (1965).
(7) Bailey, G. W., Karickhoff, S. W., *Anal. Lett.*, **6,** 43 (1973).
(8) Carey, J. H., Lawrence, J., Tosine, H. M., *Bull. Environ. Contam. Toxicol.*, **16,** 697 (1976).
(9) Fatiati, A. J., *Environ. Sci. Technol.*, **1,** 570 (1967).
(10) McGinnes, P. R., Ph.D. Thesis, University of Illinois, Urbana-Champaign, Ill., 1974.
(11) Andelman, J. B., Suess, M. J., in "Organic Compounds in Aquatic Environments", S. J. Faust, J. V. Hunter, Ed., Marcel Dekker, New York, 1971, pp 439–68.
(12) Miller, G. C., Zepp, R. G., *Water Res.*, in press.
(13) Jackson, M. L., "Soil Chemical Analysis, Advanced Course", University of Wisconsin Press, Madison, Wis., 1956, pp 110–15.
(14) Wagner, P. J., Kelso, P. A., Zepp, R. G., *J. Am. Chem. Soc.*, **94,** 7480 (1972).
(15) Zepp, R. G., Wolfe, N. L., Azarraga, L. V., Cox, R. H., Pape, C. W., *Arch. Environ. Contam. Toxicol.*, **6,** 305 (1977).
(16) Wagner, P. J., Kelso, P. A., Kemppainen, A. E., McGrath, J. M., Schott, H. N., Zepp, R. G., *J. Am. Chem. Soc.*, **94,** 7506 (1972).
(17) Moses, F. G., Liu, R. S. H., Monroe, B. M., *Mol. Photochem.*, **1,** 245 (1969).
(18) Karickhoff, S. W., Brown, D. S., Scott, T. A., *Water Res.*, in press.
(19) Miller, G. C., Miile, M. J., Crosby, D. G., Sontum, S., Zepp, R. G., *Tetrahedron*, in press.
(20) Zepp, R. G., *Environ. Sci. Technol.*, **12,** 327 (1978).
(21) Turro, N. J., Liu, K., Chow, M., *Photochem. Photobiol.*, **26,** 413 (1977).
(22) Karickhoff, S. W., Brown, D. S., *J. Environ. Qual.*, **7,** 246 (1978).
(23) Hautala, R. R., "Surfactant Effects on Pesticide Photochemistry in Water and Soil", EPA-600/30-78-060, U.S. EPA, Athens, Ga., June 1978.
(24) Hautala, R. R., University of Georgia, Athens, Ga., unpublished results, 1977.

Received for review November 2, 1978. Accepted March 30, 1979. Mention of trade names or company products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.